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THE FORMATION AND THERMOCHEMICAL PROPERTIES
OF MULTILIGAND COMPLEXES

FINAL REPORT

August 25, 1987

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This research program constituted an investigation of the reactivity and formation of ions that are clustered by molecules. Results are reported for ion-molecule reactions involving sulfides, mercaptans, and dimethyl methylphosphonate with ionic species derived from water and argon. Rate coefficients were measured and product ions identified. Results are also reported for the competitive clustering of water and methanol onto a charged center, namely the potassium cation. The thermochemical parameters for clustering up to three ligands were determined. Relationships of the gas phase data to properties of condensed phase binary solvent systems is also discussed.

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TABLE OF CONTENTS

I. BRIEF SUMMARY OF RECENT ACCOMPLISHMENTS

Support from the U. S. Army Research Office for the grant entitled "The Formation and Thermochemical Properties of Multiligand Complexes" commenced on July 1, 1984. The general objectives of the research program have been to investigate the formation and reactivity of ions that are clustered by ligands. The emphasis of the studies on reactivity has been on reactions involving compounds relevant to the Army's Chemical Defense Program. These compounds include sulfides, mercaptans, and phosphonates for which the results may be useful in the development of detection techniques that employ ion mobility analyzers or mass spectrometers. In terms of basic science, the results are of value in furthering an understanding of the details of proton and charge transfer reactions. The intention of thermodynamic investigations has been to expand the data base for the formation of mixed cluster ions (or multiligand complexes) and to explore relationships with the thermochemistry of binary soutions in the condensed phase.

The results of this research have formed the basis for 10 publications and 17 presentations at scientific conferences. A list of these publications is attached. A brief summary of the findings is given below.

Ion-Molecule Reactions Involving Sulfides and Phosphonates

Promising techniques for the detection and monitoring of chemical agents in the field involve the use of ion mobility and mass spectrometers. Detection of a species by such instruments in an atmospheric environment requires that the species enter into the ion chemistry and that the ionic products remain detectable on the time scale of the measurement. Both natural ionization (primarily from background radioactivity) and artificial means ionize components in the air which then may eventually involve trace species

of interest. In this case, introduction of such a trace species into the environment will modify the mobility or mass spectra. Recent measurements by Eisele (1) have shown variability in the positive ion spectra of naturally occurring ions. These observations have been suggested (2) to be the result of the reactivity of $NH_4^+(H_2O)_n$ cluster ions with trace levels (part per trillion) of high proton affinity species such as pyridine and picolines.

We have constructed a facility that enables a study of the kinetics of ion-molecule reactions. In the selected ion flow tube (SIFT) apparatus, ions are produced, typically in our experiments thus far, by electron impact ionization of an adiabatic expansion. Ions of a particular mass-to-charge ratio are selected with a quadrupole mass filter and injected into the flow tube. Reactant gases can be added at any inlet position in the flow tube, so kinetic data can be determined by varying the position of reactant injection, by varying the bulk flow velocity or, as usual, by varying the flow rate of reactant gas into the flow tube.

The ion densities are much lower than the concentration of the neutral reactant gas and conditions are established so that the reactions proceed via pseudo-first order kinetics. Rate coefficients are obtained from the slope of the natural logarithm of the measured signal intensty of the reactant ion versus the flow rate of reactant gas. Other necessary parameters are the flow velocity of the ions, the reaction distance, the flow rate of carrier gas and the average pressure in the flow tube. Further details of the instrument and experimental procedure are given in References (3) and (4).

The first task upon completion of the construction of the apparatus was to examine the reproducibility and accuracy of the results through a series of diagnostic tests. The effects of instrumental design such as different flow tube diameters, reactant gas inlet designs, and sampling configurations were

studied, as detailed in Reference (3), for the reactions of a simple atomic ion Ar^+ whose reaction rates (particularly with O_2) were presumably well-known. Although reproducibility of a given instrumental system is usually within 5%, we traced the source of system-to-system discrepancies of up to 30% to systematic errors due to variations in the size of the reaction tube and reactant gas inlets. We discovered systematic errors to be particularly onerous if the flow tube diameter is less than about 7 cm. These systematic errors were exacerbated with certain inlet designs (e.g., point sources) and shorter reaction times (i.e., shorter reaction zones or faster bulk flow rates).

As a consequence of a study (under the sponsorship of another agency) involving the charge transfer reactions of Ar^+ and Ar_2^+ with several species (4,5), we selected these ions as a first case for ionic reactants in reaction with neutral species such as sulfides and mercaptans which are of interest to the Army. The results are given in a paper submitted to the International Journal of Mass Spectrometry and Ion Processes. This paper is attached as Appendix A. This study was extended to include reactions with ions derived from water, namely H_xO^+ (x=1, 2, or 3), and these results are also reported in Appendix A. All the measured rate coefficients indicate that the reactions occur upon nearly every collision.

The reactions of DMMP with H_3O^+, H_2O^+, Ar^+, and Ar_2^+ were also examined. In the case of Ar^+ and Ar_2^+, the rate coefficients were found to be, respectively, 0.7×10^{-9} and 1.4×10^{-9} cm^3 s^{-1}. We have also identified the ionic products of these reactions. Charge transfer produces $DMMP^+$ (mass 124). Some of the protonated species $DMMPH^+$ (mass 125) is also observed as a consequence of secondary reactions. In addition, products which correspond to fragments of DMMP are observed. The most notable of these is mass 79

corresponding to the loss of a methyl radical and formaldehyde. Smaller amounts, particularly in the reaction with Ar^+, of mass 63, 94, and 109 corresponding to CH_3PCH^+, $CH_3OPOH^+(CH_3)$, and $CH_3OP(O)_2CH_3^+$ are also found. The greater fragmentation with Ar^+ reactions correlates with a greater exothermicity of the charge transfer reactions. Similar fragmentation has been observed in collision-induced dissociation and electron impact ionization mass spectrometry of DMMP by Holtzclaw et al. (6).

We have determined that H_2O^+ and H_3O^+ react with DMMP with rate coefficients of 4.8×10^{-9} and 1.9×10^{-9} cm^3 s^{-1}, respectively. The ion H_2O^+ has available both charge and proton transfer channels. The product ion at mass 94, as well as $DMMP^+$ and $DMMPH^+$ are present in the product distribution. With H_3O^+, on the other hand, only the proton transfer product $DMMPH^+$ is observed.

In normal air, ions become hydrated after formation, so that an assessment of the effect of the extent of hydration of an ion on its reactivity is necessary. For the reaction

$$AH^+(H_2O)_n + B \rightarrow BH^+(H_2O)_m + (n-m)H_2O + A$$
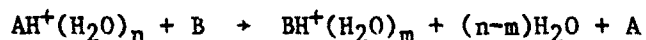
m may take on values between 0 and n. The relative values of m and n can affect whether a reaction will occur. Solvation of an ion tends to stabilize the ion. Consequently, the proton affinity difference between A and B, the degree of hydration of AH^+ and the ability of the product ion BH^+ to retain the H_2O solvent molecules influences the rate of reactions.

The proton affinity of DMMP is at least 40 kcal/mol greater than that of water. (DMMP has a proton affinity greater than NH_3.) The hydration energy of H_3O^+ by one, two, and three water molecules is 32, 52, and 69 kcal/mol, respectively. Consequently the proton transfer reaction of DMMP with at least

$H_3O^+ \cdot H_2O$ remains exothermic, even without hydration of DMMPH$^+$. The rate coefficients for the reactions of DMMP with $H_3O^+(H_2O)_n$ for n=1 to 3 were measured to be about 9×10^{-10} cm^3 sec^{-1} for all three hydrates. This value is about half of that obtained for the bare ion H_3O^+, but still reasonably fast. The observed products were DMMPH$^+$ and DMMPH$^+ \cdot H_2O$. No greater hydration of DMMPH$^+$ was evident in these experiments.

As an alternate method of detection, chemiluminescence due to ion-molecule reactions is of interest. As an example, visible light emission is observed with the addition of CS_2 to a flowing Ar afterglow. This emission has been identified as the $A^2\Pi_u$ to the $X^2\Pi_g$ transition of CS_2^+. Endoh and coworkers (7) identified an ionic species of Ar as the excitation source of CS_2^+ into the A state. Due to the energetics involved and experiments where an increase in the chemiluminescence intensity was observed as the pressure of Ar was increased, they concluded that the excitation source was due to the charge transfer reaction, $Ar_2^+ + CS_2 \rightarrow CS_2^+(A^2\Pi_g) + 2Ar$. In contrast to this work, the results of our study (8) demonstrate that the excitation source is Ar$^+$.

This study occurred under plasma conditions in which a number of species are energetically capable of forming $CS_2^+(A^2\Pi_u)$. Electrons are eliminated as a possible excitation source since their energy following the glow discharge is typically 2-8 eV, too low for the production of $CS_2^+(A)$ by electron impact. Ar_2^{+*} has also been neglected due to the fact that Ar_2^+ is formed by a termolecular association reaction where a third body is necessary to stabilize the complex and remove the excess energy. Excited neutral species were shown not to be responsible for the chemiluminescence by verifying that the light intensity dropped when ions were prevented electrostatically from travelling down the flow tube to the interaction zone.

The apparatus is equipped with a roots pump containing a continuously variable gate valve which enables the pressure and flow velocity to be changed independently of one another. When the pressure in the flow tube was increased while the flow velocity was maintained constant, the intensity of chemiluminescence remained relatively constant. However, the intensity of Ar_2^+, which was also monitored, was found to increase with pressure suggesting that Ar_2^+ was not the excitation source.

When the flow velocity was increased and the pressure was fixed, there was a significant increase in the light emission. Since the reaction time is inversely proportional to the flow velocity, less Ar_2^+ formation from the association reaction $Ar^+ + Ar + M \rightarrow Ar_2^+ + M$ was observed at higher velocities. These two experiments indicate that Ar^+, not Ar_2^+, is the excitation source.

Thermochemistry of Multiligand Cluster Ions

One of the motivations for research on cluster ions is the parallel that the growth of cluster ions has with phenomena such as nucleation and solvation. For instance, the thermodynamics involved in the clustering of molecules about ions have been related to single ion heats of solvation (9). Most studies of clustering in the gas phase have been concerned with the sequential attachment of one particular species to an ion. Few studies of competitive clustering by two different solvent species to yield mixed solvent cluster ions have been performed. In such systems, clustering may be enhanced or hindered by solvent-solvent interactions. The question also arises as to the composition of the solvent in the immediate neighborhood of the solute and the extent to which it differs from the bulk solution. Furthermore, the environment, as for example the natural atmosphere, is such

that mixed cluster ions are prevalent. The purpose of this phase of the program has been to expand the data base for the thermodynamics of the competitive clustering of gas phase ions by two different substances and to explore relationships with condensed phase binary solutions. Specifically, we have chosen to investigate the competitive clustering of water and methanol onto the potassium ion K^+ and the chloride ion Cl^-.

The results were obtained by using a high pressure ion source mass spectrometer. The instrument and the experimental procedure for determining the enthalpy, entropy, and free energy changes of clustering reactions have been described in detail elsewhere (10). The measured thermodynamic quantities for the $K^+/CH_3OH/H_2O$ system are listed in Table 1 of Appendix B. Work on the $Cl^-/CH_3OH)H_2O$ system is still in progress, but nearing completion. Results from the latter system will expose any effects due to the polarity of the solute in the methanol/water system.

In regard to binary solvents, a perspective is gained by considering the total heat of clustering, $-\Delta H_{fc}^o$, for the reaction $I + mA + nB \rightarrow I(A)_m(B)_m$ as a function of the mole fraction of one of the solvents and cluster size. This representation is shown in Figure 2 of Appendix B for data on four different systems. The solid lines indicate the compositionally weighted average of the pure systems for a given cluster size. The two cases for which a strong interaction between the two solvent species is known, i.e., SO_2 in H_2O and NH_3 in H_2O, show a significant deviation of the heat of clustering above the weighted average. In the case of NH_4^+, with NH_3/H_2O, the heat of clustering for $NH_4^+(NH_3)_3(H_2O)$ is greater than that for either of the pure clusters. The upward deviation also appears to increase with increasing cluster size as might be expected since solvent-solvent

interactions should play an increasingly important role as the number of solvent molecules increase. For the methanol/water system, in which the heat of mixing in the condensed phase is relatively small, no consistent trends in deviations are noticeable. For benzene/water, for which mutual solubility is limited, a slight downward deviation from the weighted average is apparent. Hence, comparison of the total heat of clustering onto a gas-phase ion with the compositionally weighted average value follows trends that might be expected based on the properties of the condensed binary solvents.

II. BIBLIOGRAPHY

1. M. D. Perkins and F. L. Eisele, J. Geophys. Res. $\underline{89}$, 9646 (1984); F. L. Eisele and E. W. McDaniel, J. Geophys. Res. $\underline{91}$, 5183 (1986).

2. R. G. Keesee and A. W. Castleman, Jr., J. Geophys. Res. $\underline{90}$, 5885 (1985).

3. B. L. Upschulte, R. J. Shul, R. Passarella, R. G. Keesee, and A. W. Castleman, Jr., Int. J. Mass Spectrom. Ion Proc. $\underline{75}$, 27 (1987).

4. R. J. Shul, B. L. Upschulte, R. Passarella, R. G. Keesee, and A. W. Castleman, Jr., J. Phys. Chem. $\underline{91}$, 2556 (1987).

5. R. J. Shul, R. Passarella, B. L. Upschulte, R. G. Keesee, and A. W. Castleman, Jr., J. Chem. Phys. $\underline{86}$, 4446 (1987).

6. J. R Holtzclaw, J. R. Wyatt, and J. E. Campana, Org. Mass Spect. $\underline{20}$, 90 (1985).

7. M. Endoh, M. Tsuji, and Y. Nishimura, Chem. Phys. Lett. $\underline{109}$, 35 (1984).

8. B. L. Upschulte, R. J. Shul, R. Passarella, R. L. Leuchtner, R. G. Keesee, and A. W. Castleman, Jr., J. Phys. Chem. $\underline{90}$, 100 (1986).

9. N. Lee, R. G. Keesee, and A. W. Castleman, Jr., J. Coll. Interface Sci. $\underline{75}$, 555 (1980).

10. A. W. Castleman, Jr., P. M. Holland, D. M. Lindsay, and K. I. Peterson, J. Am. Chem. Soc. $\underline{100}$, 6039 (1978).

III. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED
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Title of Thesis: "The Kinetic Study of Gas Phase Ion-Molecule
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IV. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP

"Gas Phase Reactions of Sulfides, Mercaptans, and Dimethyl Methyl-phosphonate With Ionic Species Derived from Argon and Water," R. Passarella, R. J. Shul, R. G. Keesee, and A. W. Castleman, Jr., Int. J. Mass Spectrom. Ion Proc., submitted.

"The Thermodynamics of Mixed Solvent Cluster Ions: $K^+(CH_3OH)_n(H_2O)_m$," R. G. Keesee, D. H. Evans, and A. W. Castleman, Jr., Proc. Int. Symposium on the Physics and Chemistry of Small Clusters, Richmond, VA, October 28-November 1, 1986, in press.

"The Ion-Molecule Reactions of Sulfides and Phosphonates," R. G. Keesee and A. W. Castleman, Jr., Proc. 1986 CRDC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November 18-21, Vol. 2, pp. 785-789 (1987).

"Clusters: Bridging the Gas and Condensed Phases," A. W. Castleman, Jr. and R. G. Keesee, Accts. Chem. Res. 19, 413 (1986).

"Ionic Clusters," A. W. Castleman, Jr. and R. G. Keesee, Chem. Rev. 86, 589 (1986).

"Reaction of Sulfur Containing Compounds with Atmospheric Ions," A. W. Castleman, Jr. and R. G. Keesee, Proc. CRDC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November 19-22, pp. 669-674 (1986).

"Chemiluminescence of CS_2^+ Initiated by a Thermal Energy Charge Transfer Reaction with Ar^+," B. L. Upschulte, R. J. Shul, R. Passarella, R. E. Leuchtner, R. G. Keesee and A. W. Castleman, Jr., J. Phys. Chem. 90, 100 (1986).

"Studies of Charge Transfer Processes in a Flow Tube," R. G. Keesee, B. L. Upchulte, R. J. Shul, R. Passarella, R. E. Leuchtner, and A. W. Castleman, Jr., Proc. 14th International Conference on the Physics of Electronic and Atomic Collisions, July 24-30, Palo Alto, CA, p. 588 (1985).

"One- and Two-Color Resonance Enhanced Multiphoton Ionization of van der Waals Molecules: Studies of Spectroscopic Shifts as a Function of Degree of Aggregation," A. W. Castleman, Jr., P. D. Dao, S. Morgan, and R. G. Keesee, Proc. 14th International Conference on the Physics of Electronic and Atomic Collisions, July 24-30, p. 655 (1985).

"Mass Spectrometric and Chemiluminescent Studies of CS_2^+ in a Flowing Argon Afterglow," R. J. Shul, B. L. Upschulte, R. Passarella, R. E. Leuchtner, R. G. Keesee and A. W. Castleman, Jr., Proc. 33rd Annual ASMS Meeting, May 26-31, San Diego, CA, pp. 146-147 (1985).

Gas Phase Reactions of Sulfides, Mercaptans, and Dimethyl
Methylphosphonate with Ionic Species Derived from Argon and Water[‡]

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ABSTRACT

Rate coefficients for gas phase ion-molecule reactions involving dimethyl methylphosphonate (DMMP), sulfides, and mercaptans of the form RSR' (where R = H, CH_3, CH_3CH_2) are measured by using a selected ion flow tube (SIFT) technique. The ionic reactants include Ar^+, Ar_2^+, OH^+, H_2O^+, $H_3O^+(H_2O)_n$ with n = 0 to 3. All the rate coefficients indicate relatively fast, nearly collisional, reactions. Ar^+ and Ar_2^+ react with DMMP to produce the parent ion (charge transfer channel) as well as ionic fragments of DMMP. Reactions of DMMP and RSR' with H_3O^+ result in proton transfer. Both proton and charge transfer products are observed when H_2O^+ reacts with DMMP. Hydration of H_3O^+ by up to three water molecules reduces the proton transfer reaction rate with DMMP by a factor of two.

INTRODUCTION

Phosphates are species of major importance in biological systems (2) and organophosphorus compounds are also present in detergents and flame retardants and find use in the agricultural industry as pesticides and fertilizers (3). The chemistry of sulfur compounds is important with regard to the burning of fossil fuels and the subsequent environmental impact. Organic sulfur compounds occur in practically all living matter, for example as components of proteins, and yet can also be detrimental; methyl mercaptan acts on the central nervous system of fish to produce paralysis. The study of mercaptans is also important since they are often used as starting materials for making plastics, wetting agents, pharmaceuticals, and insecticides (4).

Many of these compounds or their derivatives and degradative products are either highly toxic or they adversely affect the environment (5). Thus, the trace analysis of the phosphorus and sulfur-containing species in the biosphere is of great importance. Promising methods of detection include mass spectrometric techniques such as positive and negative ion-chemical ionization (6) and field desorption mass spectrometry (7). In addition, understanding the role of electric discharges in air purification systems (8) requires information on the ion-molecule chemistry of these species.

The ionic species in the atmosphere are determined by the neutral composition of the environment. Both natural (primarily from background radioactivity) and artificial means produce ionized components in air that may transfer charge through a series of ion-molecule reactions. Recent measurements by Eisele and co-workers (9) have shown variability in the positive ion mass spectra of naturally occurring ions. These observations have been suggested (10,11) to be the result of the reactivity of $NH_4^+(H_2O)_n$ cluster ions with trace levels (part per trillion) of high proton affinity species such as pyridine and picolines, which are present in natural sources such as coal tars. Detection of phosphorus and sulfur compounds by similar techniques requires that the species enter into the ion chemistry and that the ionic products retain phosphorus or sulfur atoms and remain detectable on the time scale of the measurement; thus, the limit of detection of trace species is determined by lifetime of the charged species against neutralization processes and the reaction rate of the trace species of interest with the charged species.

This paper reports results on reactions involving dimethyl methyl-phosphonate (DMMP) and sulfides and mercaptans of the form RSR' (where R = H, CH_3, or CH_3CH_2). The ionic reactants include Ar^+, Ar_2^+, OH^+, H_2O^+, and $H_3O^+(H_2O)_n$ with n = 0 to 3. The work reported herein represents a continuation of previous investigations from our laboratory in which study of the atomic and molecular argon ions is designed to elucidate factors governing charge transfer (12,13) and the study of H_xO^+ is providing data for astrophysical and atmospheric applications (14). Reactions involving the cluster ions are also important in developing a fundamental understanding of reactions in solutions (15,16).

EXPERIMENTAL

The selected ion flow tube (SIFT (17)) apparatus used in our laboratory has been described previously (12); therefore, only the details pertaining to the present study are discussed. The reactant ions are produced by electron impact on a free jet expansion of either argon or a $He-H_2O$ gas mixture into vacuum. The ions are focused into the SIFT quadrupole mass spectrometer, whereupon the desired species is mass selected from the distribution of ions and injected into the flow tube. The injected ions are thermalized by collisions with the carrier gas (helium) and are allowed to react with the neutral reactant gas which is added at an appropriate downstream location (18). The rate coefficients are obtained in the conventional manner by monitoring the intensity of the reactant ion of interest, with a quadrupole mass spectrometer, as a function of the concentration of the neutral reactant gas in the flow tube. The appearance of product ions is also determined mass spectrometrically. Operation of the SIFT quadrupole under high resolution is necessary to mass filter the three H_xO^+ reactant ions produced in the source. Such settings were found to reduce the injection efficiency of the desired ionic species to a point where reliable kinetic data could not be obtained. Therefore, the H_xO^+ species are injected at somewhat reduced resolution which results in the simultaneous injection into the flow tube of the three ions OH^+, H_2O^+, and H_3O^+ (14), but with a dominating concentration of the desired species. In the case of the protonated water clusters $H_3O^+(H_2O)_n$, water vapor is introduced at the beginning of the flow tube to convert H_2O^+ and H_3O^+ into the desired water clusters.

The neutrals are all obtained from the vapors of the distilled liquids except for H_2S which was commercial grade Union Carbide prepurified (99.9%

minimum) with no further purification. Residual impurities are condensed out of the He carrier gas by passing it through a sequence of three traps containing molecular sieves that are placed in liquid nitrogen.

RESULTS AND DISCUSSION

Rate coefficients for ion-molecule reactions

$$A^+ + B \rightarrow \text{products} \tag{1}$$

are determined from pseudo-first order kinetics, since typically the concentration of B greatly exceeds that of A^+. Consequently, the following equation is obtained,

$$[A^+] = [A^+]_0 \exp(-C_2 \, k \, [B] \, z/v) \tag{2}$$

where $[A^+]$ and $[A^+]_0$ are the measured intensity of A^+ with and without the presence of the neutral reactant at concentration [B], z is the distance between the reactant injection point and the sampling orifice, v is the flow velocity of the ion (measured directly by ion pulsing techniques (12-14)), C_2 is a correction factor which is due to flow dynamics (19), and k is the binary reaction rate coefficient. Typically, k is determined from the slope of $\ln([A^+]/[A^+]_0)$ versus [B] since the other values, C_2, z, and v, are known. The rate coefficients determined for the investigated reactions are given in Tables I and II. All the rate coefficients indicate relatively fast, nearly collisional, reactions.

In the reactions of Ar^+ and Ar_2^+ with $(CH_3O)_2P(O)CH_3$, abbreviated as (DMMP), several product ions are observed. The predominant ionic products are the molecular ion $DMMP^+$ (m/z 124) and a fragment ion at m/z equal to 79 which corresponds to loss of a methyl radical and formaldehyde (5). Each of these

product ions accounts for about 30 to 35% of the total product ion distribution. (No correction for mass discrimination is considered in reporting these percentages.) Two other products (m/z = 94 and 109) each account for about 10 to 15% of the product ions. Ions that contribute about 1 to 5% of the product distribution are the methoxy ion CH_3O^+ (m/z = 31), the protonated molecular ion $DMMPH^+$ (m/z = 125), and CH_4PO^+ (m/z = 63).

The recombination energies of Ar^+ and Ar_2^+ are 15.7 and 14.4 eV, respectively (12). The appearance potentials of observed ions from DMMP are reported to be 10.5, 13.4, 11.5, 13.3, 13.8, and 16.9 eV for masses 124, 79, 94, 109, 31, and 63, respectively (20). The protonated species $DMMPH^+$ is necessarily the consequence of secondary reactions involving proton transfer from primary product ions to DMMP. In view of the reported appearance potentials, mass 63 also probably results from secondary reactions. Interestingly, similar fragment ions have been seen in collision-induced dissociation and electron impact ionization mass spectrometry of DMMP by Holtzclaw et al. (5). In particular, they report the major fragments are masses 109, 94, and 79 amu and suggest that a keto-enol isomerization of the DMMP molecular ions explain these fragmentation patterns.

When H_2O^+ reacts with DMMP both the charge transfer and the proton transfer products, $DMMP^+$ and $DMMPH^+$, are observed. The fragment at m/z 94 is also present; however, no other fragments are seen. Since the recombination energy of H_2O^+ is only 12.6 eV, mass 94 is the only possible fragmentation channel (the appearance potentials for the fragment ions from DMMP are given above). With the H_3O^+ ion, only the proton transfer product $DMMPH^+$ is observed.

In air, ions can become hydrated after formation. In order to assess the effect of the extent of hydration on reaction with H_3O^+, the cluster ions $H_3O^+(H_2O)_n$ reactions were examined. For the reaction

$$H_3O^+(H_2O)_n + B \rightarrow BH^+(H_2O)_m + (n - m+1)H_2O \qquad (3)$$
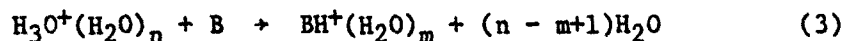
where m may take on values from 0 to n. Solvation of an ion tends to stabilize the ion. The proton affinity difference between H_2O and B, the degree of hydration of H_3O^+ and the ability of the product ion BH^+ to retain the H_2O solvent molecules (bond energy), influences the rate of reaction (21).

Based on the similarity of DMMP with $(CH_3O)_3P$ and $(CH_3O)_3PO$ which have proton affinities of 9.6 and 9.2 eV, respectively (22), the proton affinity of DMMP is expected to be about 2 eV greater than that of water. The hydration energy of H_3O^+ by 1, 2, and 3 water molecules is 1.4, 2.2, and 3.0 eV, respectively (23). Consequently, the proton transfer reaction of DMMP with at least $H_3O^+ \cdot H_2O$ remains exoergic, even without the hydration of $DMMPH^+$. The rate coefficients for the reactions of DMMP with $H_3O^+ \cdot (H_2O)_n$ for n = 1 to 3 were measured to be about 9×10^{-10} cm^3 s^{-1} (see Table II) for all three hydrates. This value is about half of that obtained for the bare ion, H_3O^+, but still reasonably fast. The observed products are $DMMPH^+$ and $DMMPH^+ \cdot H_2O$. No greater hydration of DMMP is evident in these experiments.

The reactions involving Ar^+ and Ar_2^+ with sulfides and mercaptans proceed via a charge transfer reaction, except H_2S which proceeds as a proton transfer reaction, to yield the primary product ion RSR'. At higher concentrations of the neutral reactant, secondary reactions yield protonated monomer and dimer product ions.

The ions H_3O^+, H_2O^+, and OH^+ undergo proton transfer reactions upon nearly every collision with H_2S, CH_3SH, CH_3CH_2SH, and $(CH_3)_2S$. Although charge transfer is also energetically accessible in the case of reactions with H_2O^+ and OH^+, proton transfer is always the dominant channel. In the reactions of H_3O^+ with RSR' the rate coefficients increase in the order H_2S, CH_3SH, CH_3CH_2SH, $(CH_3)_2S$. The difference in proton affinity between RSR' and H_2O also follows the same trend 0.16, 0.91, 1.1, and 1.5 eV, respectively (22). Hydrogen sulfide which has the smallest proton affinity difference has the smallest rate coefficient. In accordance with a reaction rate corresponding to a collision frequency, the rate coefficients increase slightly from H_3O^+ to H_2O^+ to OH^+ due to the decrease in mass of the ion.

CONCLUSIONS

The reactions of DMMP and RSR' with H_3O^+ are rapid and result in proton transfer. Hydration of H_3O^+ by up to three water molecules reduces the proton transfer reaction rate with DMMP by only a factor of two. Charge transfer reactions of DMMP with Ar^+, Ar_2^+, and H_2O^+ lead to product ions corresponding to fragments of DMMP as well as the parent ion.

ACKNOWLEDGMENTS

References

1. E. E. Ferguson, F. C. Fehsenfeld and A. L. Schmeltekopf, Adv. Atom. Mol. Phys. 5, 1 (1969).

2. F. H. Westheimer, Science 235, 1173 (1987).

3. J. Emsley and D. Hall, The Chemistry of Phosphorus, Harper and Row, New York, 1976.

4. E. E. Reid, Organic Chemistry of Bivalent Sulfur, Vol. 1, Chemical Publishing Co., Inc., New York, 1958.

5. J. R. Holtzclaw, J. R. Wyatt and J. E. Campana, Organic Mass Spectrometry 20, 90 (1985).

6. T. Hudec, J. Thean, D. Kuehl and R. C. Doughterty, Science 211, 952 (1981).

7. J. N. Damico, R. P. Barron and J. A. Sphon, Int. J. Mass Spectrom. Ion Phys. 2, 161 (1969).

8. M. E. Fraser, H. G. Eaton and R. S. Sheinson, Environ. Sci. Technol. 19, 946 (1985).

9. M. D. Perkins and F. L. Eisele, J. Geophys. Res. 89, 9646 (1984); F. L. Eisele and E. W. McDaniel, J. Geophys. Res. 91, 5183 (1986).

10. R. G. Keesee and A. W. Castleman, Jr., J. Geophys. Res. 90, 5885 (1985).

11. F. L. Eisele, J. Geophys. Res. 91, 7897 (1986).

12. R. J. Shul, B. L. Upschulte, R. Passarella, R. G. Keesee and A. W. Castleman, Jr., "Thermal Energy Charge Transfer Reactions of Ar^+ and Ar_2^+," J. Phys. Chem., in press.

13. R. J. Shul, R. Passarella, B. L. Upschulte, R. G. Keesee and A. W. Castleman, Jr., J. Chem. Phys. 86, 4446 (1987).

14. R. J. Shul, R. Passarella, L. T. DeFazio, Jr., R. G. Keesee and A. W. Castleman, Jr., "Ion-Molecule Reactions Involving H_3O^+, H_2O^+, and OH^- at Thermal Energy," submitted.

15. A. W. Castleman, Jr. and R. G. Keesee, Acct. Chem. Res. 19, 413 (1986).

16. A. W. Castleman, Jr. and R. G. Keesee, Chem. Rev. 86, 589 (1986).

17. D. Smith and N. G. Adams, in Gas Phase Ion Chemistry, Vol. 1, M. T. Bowers, Ed., Academic Press, New York, pp. 1-44 (1979).

18. B. L. Upschulte, R. J. Shul, R. Passarella, R. G. Keesee and A. W. Castleman, Jr., "Diagnostics of Flow Tube Techniques for Ion-Molecule Reactions," Int. J. Mass Spectrom. Ion Proc., in press.

19. N. G. Adams, M. J. Church and D. Smith, J. Phys. D: Appl. Phys. 8, 1409 (1975).

20. D. A. Bafus, E. J. Gallegos and R. W. Kiser, J. Phys. Chem. 70, 2614 (1966).

21. D. K. Bohme, NATO Adv. Study Inst. Series C, Vol. 118, 111 (1984).

22. S. G. Lias, J. F. Liebman and R. D. Levin, J. Phys. Chem. Ref. Data 13, 695 (1984).

23. A. J. Cunningham, J. D. Payzant and P. Kebarle, J. Am. Chem. Soc. 94, 7627 (1972).

Table I

Rate Coefficients in 10^{-9} cm^3 s^{-1} for Ion-Molecule Reactions

Neutral/Ion	Ar$^+$	Ar$_2^+$	OH$^+$	H$_2$O$^+$	H$_3$O$^+$
DMMP	0.65	1.4	----	4.8	1.9
H$_2$S	1.3	1.2	1.6	1.5	1.4
CH$_3$SH	1.7	1.5	1.1	1.1	1.0
CH$_3$CH$_2$SH	2.1	1.9	3.5	3.3	3.0
(CH$_3$)$_2$S	1.6	1.8	2.3	2.1	2.1

Table II

Rate Coefficients for the Reactions
$H_3O^+(H_2O)_n$ with DMMP

n	k (10^{-9} cm^3 s^{-1})
0	1.9
1	0.9
2	0.9
3	0.8

THE THERMODYNAMICS OF MIXED SOLVENT CLUSTER IONS: $K^+(CH_3OH)_n(H_2O)_m$

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INTRODUCTION

One of the motivations for research on cluster ions is the parallel that the growth of cluster ions has with phenomena such as nucleation[1,2] and solvation.[3,4] For instance, the thermodynamics involved in the clustering of molecules about ions have been related to single ion heats of solvation.[5,6] Most studies of clustering have been concerned with the sequential attachment of one particular species to an ion, as evident in a recent compilation[7] of thermodynamic data on clusters ions. Few studies of competitive clustering by two different solvent species to yield mixed solvent cluster ions have been performed. In such systems, clustering may be enhanced or hindered by solvent-solvent interactions. Furthermore, the environment, as for example the natural atmosphere,[8] is such that mixed cluster ions are prevalent and data for single component systems is inadequate. The purpose of this study is to expand the data base for binary solvent systems and to explore relationships with condensed phase binary solutions. Specifically, we have chosen to investigate the competitive clustering of water and methanol onto the potassium ion K^+.

EXPERIMENT AND RESULTS

The results were obtained by using a high pressure ion source mass spectrometer. The instrument and the experimental procedure for determining the enthalpy, entropy, and free energy changes of clustering reactions have been described previously.[9]

The measured thermodynamic quantities for the $K^+/CH_3OH/H_2O$ system are listed in Table 1. For the association reactions of H_2O onto $K^+(CH_3OH)$ and $K^+(CH_3OH)(H_2O)$, the water partial pressure in the ion source was determined by monitoring the $K^+(H_2O)_n$ intensities and using the well-known equilibrium constants for K^+ hydration[10] to calculate the water partial pressure. This procedure greatly reduced the scatter in the data for these reactions which was apparently caused by absorption of water on the walls of the instrument.

Consistency of the data can be verified whenever the thermochemical properties of a cluster ion can be traced via two independent routes. For example, the formation of $K^+(CH_3OH)_2(H_2O)$ from $K^+(CH_3OH)$, CH_3OH, and

Table I

The Thermodynamic Quantities for the Association Reaction
I + B → I(B) in the K⁺/CH₃OH/H₂O System

I	B	$-\Delta H^\circ$ (kcal/mol)	$-\Delta S^\circ$ (cal/K mol)	$-\Delta G^\circ_{298}$ (kcal/mol)	Ref
K⁺	H₂O	17.9	21.6	11.5	[10]
K⁺(CH₃OH)	CH₃OH	18.0	35	7.6	*
K⁺(CH₃OH)	H₂O	15.6	22.5	8.9	*
K⁺(H₂O)	CH₃OH	19.6	32.5	9.9	*
K⁺(H₂O)	H₂O	16.1	24.2	8.9	[10]
K⁺(CH₃OH)₂	CH₃OH	14.5	28	6.2	*
K⁺(CH₃OH)₂	H₂O	11.3	18.0	5.9	*
K⁺(CH₃OH)(H₂O)	CH₃OH	13.5	27.3	5.4	*
K⁺(CH₃OH)(H₂O)	H₂O	13.1	22.5	6.4	*
K⁺(H₂O)₂	H₂O	13.2	23.0	6.3	[10]
K⁺(CH₃OH)₃	CH₃OH	12.5	29	3.9	*
K⁺(CH₃OH)₂(H₂O)	CH₃OH	12.5	25.6	4.9	*
K⁺(H₂O)₃	H₂O	11.8	24.7	4.4	[10]

*Present Work

H₂O can be obtained through the summation of data for the pair of equilibria

$$K^+(CH_3OH) + CH_3OH \rightleftharpoons K^+(CH_3OH)_2$$

$$K^+(CH_3OH)_2 + H_2O \rightleftharpoons K^+(CH_3OH)_2(H_2O)$$

to yield -29.3 kcal/mol and -53.0 cal/K·mol, for ΔH° and ΔS°, respectively. These values compare well with the respective values of -29.1 kcal/mol and -49.8 cal/K·mol obtained from the pair of equilibria

$$K^+(CH_3OH) + H_2O \rightleftharpoons K^+(CH_3OH)(H_2O)$$

$$K^+(CH_3OH)(H_2O) + CH_3OH \rightleftharpoons K^+(CH_3OH)_2(H_2O)$$
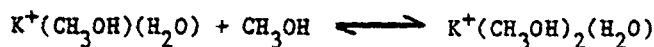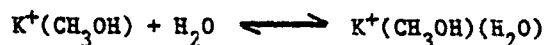
In addition to the studied reactions listed in Table 1, the thermodynamic values for other clustering reactions can be determined through the closure of thermodynamic cycles. Figure 1 depicts the clustering pathways with the respective enthalpy changes. The calculated values are indicated with an asterisk.

DISCUSSION

Some general trends in the enthalpy and free energy changes are evident. First, the successive addition reactions exhibit the usual decreasing trend in -ΔH° and -ΔG°₂₉₈ with increasing cluster size. Second, the magnitude of the enthalpy change for association of methanol
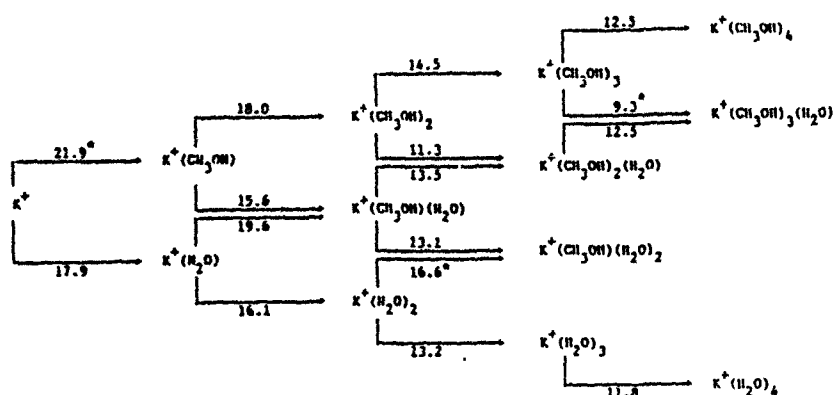
Fig. 1. Enthalpy changes $-\Delta H^\circ$ (in kcal/mol) for clustering reactions of methanol and water onto K^+.

onto a specific ion is consistently greater than that of water. This result cannot be explained by consideration of the ion-dipole interaction alone, since the dipole moment of water is slightly larger than that of methanol (1.85 versus 1.70 debye). The average polarizability of methanol, however, is greater than that of water (3.3 versus 1.45 Å^3). The larger polarizability of methanol evidently allows the ion to induce a dipole on methanol which more than compensates for the smaller permanent dipole moment.

In regard to binary solvents, a perspective is gained by considering the total heat of clustering, $-\Delta H^\circ_{tc}$, for the reaction $I + mA + nB \rightarrow I(A)_m(B)_n$ as a function of the mole fraction of one of the solvents and cluster size. This representation is shown in Figure 2 for data on four different systems. The solid lines indicate the compositionally weighted average of the pure systems for a given cluster size. The two cases for which a strong interaction between the two solvent species is known, i.e., SO_2 in H_2O and NH_3 in H_2O, show a significant deviation of the heat of clustering above the weighted average. In the case of NH_4^+, with NH_3/H_2O, the heat of clustering for $NH_4^+(NH_3)_3(H_2O)$ is greater than that for either of the pure clusters. The upward deviation also appears to increase with increasing cluster size as might be expected since solvent-solvent interactions should play an increasingly important role as the number of solvent molecules increase. For the methanol/water system, in which the heat of mixing in the condensed phase is relatively small, no consistent trends in deviations are noticeable. For benzene/water, for which mutual solubility is limited, a slight downward deviation from the weighted average is apparent. Hence, comparison of the total heat of clustering onto a gas-phase ion with the compositionally weighted average value follows trends that might be expected based on the properties of the condensed binary solvents.

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REFERENCES

1. A. W. Castleman, Jr., Adv. Coll. Interface Sci. 10:73 (1979).
2. A. W. Castleman, Jr., P. M. Holland, and R. G. Keesee, J. Chem. Phys. 68:1760 (1978).
3. P. Kebarle, Mod. Aspects Electrochem. 9:1 (1974).
4. A. W. Castleman, Jr. and R. G. Keesee, Acc. Chem. Res., in press.
5. M. Arshadi, R. Yamadagni, and P. Kebarle, J. Phys. Chem. 74:1475 (1970).
6. N. Lee, R. G. Keesee, and A. W. Castleman, Jr., J. Coll. Interface Sci. 75:555 (1980).
7. R. G. Keesee and A. W. Castleman, Jr., J. Phys. Chem. Ref. Data 15:1011 (1986).
8. R. G. Keesee and A. W. Castleman, Jr., J. Geophys. Res. 90:5885 (1985).
9. A. W. Castleman, Jr., P. M. Holland, D. H. Lindsay, and K. I. Peterson, J. Am. Chem. Soc. 100:6039 (1978).
10. S. K. Searles and P. Kebarle, Can. J. Chem. 47:2619 (1969).
11. B. L. Upschulte, F. J. Schelling, R. G. Keesee, and A. W. Castleman, Jr., Chem. Phys. Lett. 111:389 (1984).
12. J. D. Payzant, A. J. Cunningham, and P. Kebarle, Can. J. Chem. 51:3242 (1973).
13. J. Sumner, N. Nishizawa, and P. Kebarle, J. Phys. Chem. 85:1814 (1981).